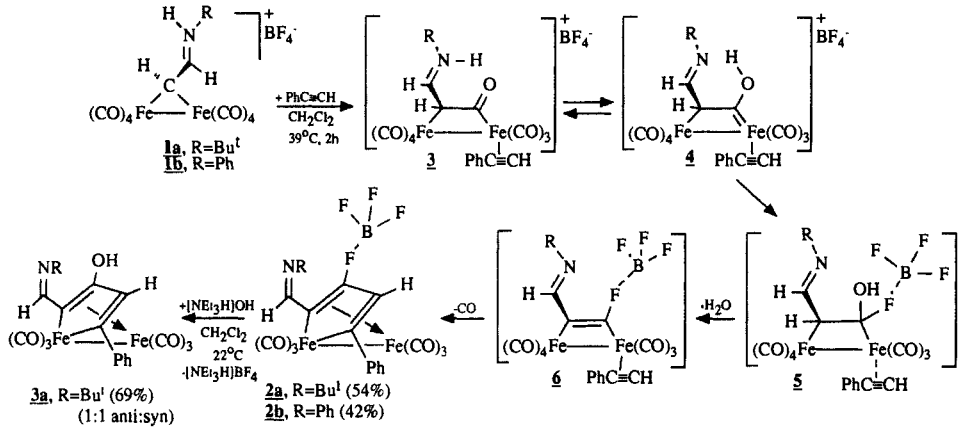
Scheme I



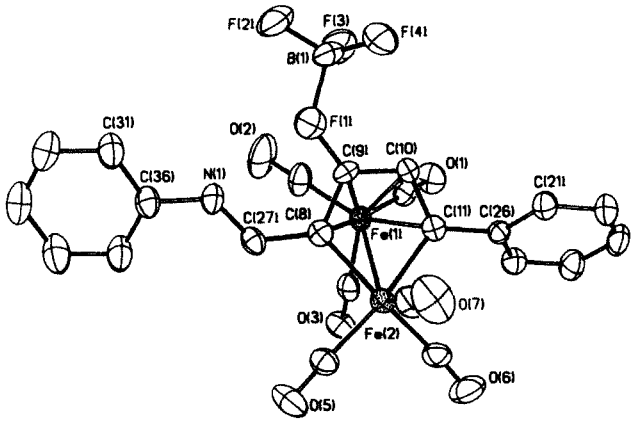


Figure 1. Molecular structure and labeling scheme for **2b** (40% thermal ellipsoids). Distances in angstroms: Fe(1)–Fe(2), 2.505 (1); Fe(1)–C(8), 2.066 (5); Fe(1)–C(9), 2.244 (5); Fe(1)–C(10), 2.171 (5); Fe(1)–C(11), 2.079 (5); Fe(2)–C(8), 1.989 (5); Fe(2)–C(11), 1.993 (5); C(8)–C(9), 1.438 (7); C(9)–C(10), 1.419 (7); C(10)–C(11), 1.422 (6); C(8)–C(27), 1.464 (7); C(27)–N(1), 1.294 (6); C(9)–F(1), 1.329 (5); F(1)–B(1), 1.528 (8); average B(1)–F(2,3,4), 1.37 (1).

The proposed mechanism for the formation of **2a,b** is shown in Scheme I. We suggest that coordination of the added alkyne induces CO insertion to form the ketene intermediate **3**, similar to the nucleophile-induced insertion of CO into the Fe–carbon bond of $Fe_2(\mu\text{-}CH_2)(CO)_8$.[7] Proton transfer from the iminium nitrogen of **3** to the carbonyl oxygen would give intermediate **4**, which could then add the BF_4^- ion to give **5**. Elimination of H_2O from **5** would form the bis(alkyne) complex **6**, which would yield the observed ferracyclopentadiene product by coupling of the two alkynes. Alternatively, water elimination could occur directly from **4** or after the ferracyclopentadiene ring had formed to give electrophilic intermediates capable of adding the BF_4^- anion. ^1H NMR analysis showed the formation of the H_2O byproduct, implying that free BF_3 is not released during the formation of **2** as otherwise this species would react with the water produced in the conversion of **1** into **2**. It was also observed that when the reaction was conducted with ^{13}CO-enriched **1a**, the product **2a** showed a significantly enhanced ^{13}C NMR resonance for the fluorine-substituted carbon atom, indicating that this carbon derived from a metal carbonyl ligand.

Although the crystal structures of **2a,b** clearly show short C–F bond lengths indicating a strong covalent bond between these atoms, preliminary reactivity studies indicate that the BF_4^- group is readily displaced by nucleophiles. When $[NEt_3H]OH$ was added to a CH_2Cl_2 solution of complex **2a**, an inseparable 1:1 mixture of syn and anti imino hydroxyferrole complexes **3a** formed, Scheme I. These complexes result from nucleophilic displacement of BF_4^- from **2a** by OH^- with subsequent imine isomerization by a tautomerization process involving proton transfer from the hydroxy group to the imine nitrogen. This reaction only occurs under basic conditions and not when just water is added to **2**. Given the apparent ease of nucleophilic displacement of the fluoride and the demonstrated transformation of ferracyclopentadiene complexes into a variety of organic products,[5a] it may prove possible to develop useful organic syntheses with complexes **2a,b**. Such studies are currently in progress.

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Sciences, for support of this work and the National Science Foundation for contributing funds toward purchase of the X-ray diffractometer at the University of Delaware.

Supplementary Material Available: Tables of atomic positional parameters for **2b**, analytical data for **2a,b**, and spectroscopic data for **2b** and **3a** (2 pages). Ordering information is given on any current masthead page.

(7) (a) Roper, M.; Strutz, H.; Keim, W. *J. Organomet. Chem.* **1981**, *219*, C5. (b) Hackenbruch, J.; Keim, W.; Röper, M.; Strutz, H. *J. Mol. Catal.* **1984**, *26*, 129.

New Trialkylsilyl Enol Ether Chemistry. Regiospecific and Stereospecific Sequential Electrophilic Addition

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In recent years much of the chemistry of enol derivatives has been dominated by the versatile reactivity of trimethylsilyl enol ethers.[1] Regiospecifically generated trimethylsilyl enol ether **1** reacts with electrophiles to give so-called kinetic products and concomitant loss of the trimethylsilyl group. The presumed oxonium intermediate **1a** is attacked by the counterion to give an "ate" complex **1b** (intermediate or transition state) leading to desilylation to give **2**. While these transformations proceed with excellent regiochemical control, the trimethylsilyl group is lost and cannot exert any further influence on the chemical fate of **2**. We have been interested in diverting the oxonium ion intermediate **1a** by proton loss rather than the usual nucleophilic attack on the silicon atom. Proton loss from **1a** should be stereospecific (axial) and result in a new regiospecifically generated trialkylsilyl enol ether. Here we report our preliminary results directed toward the above objective.[2] Treatment of the triisopropylsilyl enol ether

(1) Trialkylsilyl enol ethers have been treated with a wide range of electrophiles, see: Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 228–233. There are no examples of the direct amination of trialkylsilyl enol ethers.

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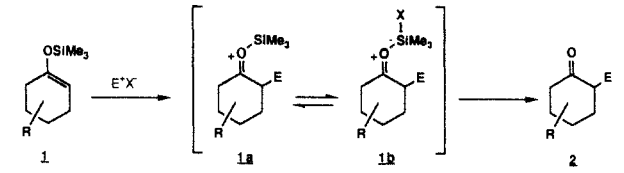
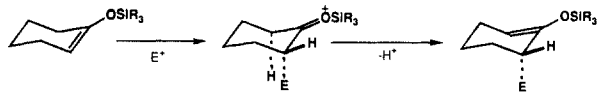
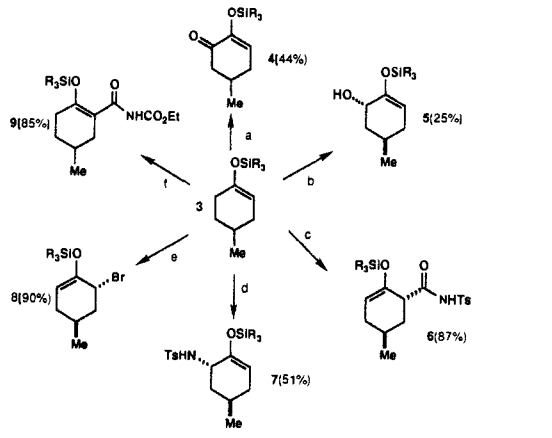
Scheme I



Scheme II

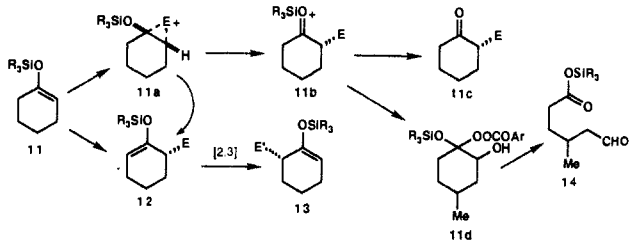


Scheme III



R=Isopropyl. a) SeO_2/DMF/RT b) SeO_2-cat./H_2O_2 c) TsNCO/RT d) TsNSeNTs/RT e) NBS/RT f) $OCNCO_2Et$/40°C

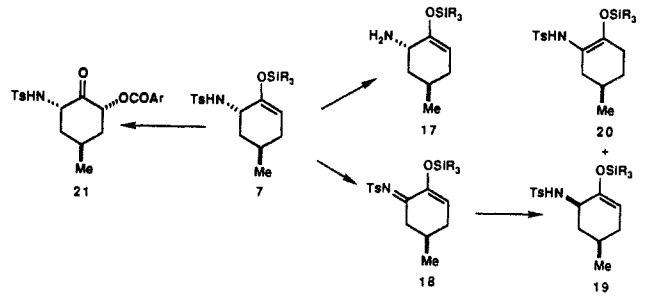
Scheme IV



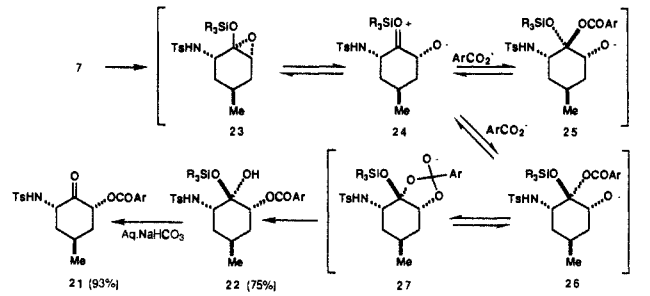
3 with a range of electrophiles gave the products shown in Scheme III. While each transformation warrants extensive discussion in terms of its particular mechanistic details, one can collectively summarize the possibilities in Scheme IV.

Electrophiles that prefer epi-ions (bromination and epoxidation) proceed via **11a** where the resulting oxonium ion **11b** can undergo proton loss to give **12** or desilylation to **11c**.[3] Interestingly if the epoxidation of **3** is carried out at −78 °C the oxonium ion **11b** is intercepted by the peracid followed by Grob fragmentation to give the aldehyde ester **14**. Equally possible is the direct conversion of **11a** into **12**. Electrophiles that react by an ene-type process (TsNCO, SeO_2, and TsNSeNTs)[4] should give **12**. If the initial adduct **12** can undergo [2.3]-sigmatropic rearrangement (SeO_2 and TsNSeNTs) **13** becomes the product. A single-crystal X-ray analysis of **7** showed the NTs group to be locked in an axial

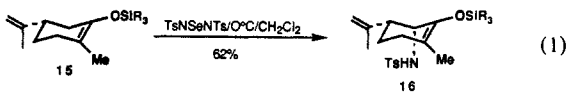
Scheme V



Scheme VI



configuration.[5] The ^1H NMR coupling pattern for the methine proton adjacent to the heteroatom in **5** and **8** also indicated an axial conformation. Treatment of (+)-dihydrocarvone triisopropylsilyl enol ether **15** with TsNSeNTs (eq 1) gave **16** as a single regio- and stereoisomer, in keeping with the pathway **12** to **13** in Scheme IV.



(1)

To illustrate some of the synthetic potential of the aminated adduct **7** we have carried out the transformations shown in Scheme V. The N–Ts bond can be reductively cleaved by Na/NH_3 to give the primary amine **17** (70%). Oxidation of **7** with SeO_2/dioxane at room temperature gave the imine **18** (90%), whereas N-halogenation of the sodium salt of **7** followed by base (NaOMe or DBU) only gave **7**. Reduction of the imine **18** with $NaBH_4$ gave only the cis-equatorial NTs adduct **19** and **20**. Exposure of **7** to MCPBA/CH_2Cl_2 at 20 °C followed by $NaHCO_3/H_2O$ gave the α-OCOAr-α-NHTs ketone **21** (70%). None of the trans diastereomer could be detected.

When **7** was treated with MCPBA/20 °C/$NaHCO_3$ the hemiacetal **22** was isolated as a moderately stable compound. Aqueous $NaHCO_3$ converted **22** into **21**. The epoxide **23** could be observed both by TLC and NMR; presumably the zwitterion **24** is trapped by the *m*-chlorobenzoate anion in a reversible manner to give **25**/**26**. Only **26** can undergo benzoyl transfer to the ortho-ester intermediate **27**, which collapses to the hemiacetal **22**.[6] NMR data show that the α-TsNH and α-OCOAr groups are axial in **22** and relax to an equatorial configuration in **21**.

We have concentrated on the NTs adduct **7** since it offers unique opportunities for the regio- and stereocontrolled manipulation of nitrogen functionality and its attendant potential for the synthesis of alkaloids. The compound **17** is a new derivative of an α-amino ketone and offers the possibility to form heterocyclic

(2) We recently reported the direct oxidation of bridgehead trialkylsilyl enol ethers related to esperamicin/calicheamicin using SeO_2. Magnus, P.; Bennett, F. *Tetrahedron Lett.* **1989**, *30*, 3637. While this work was in progress Kuwajima reported the double hydroxylation of enol silyl ethers to give α,α'-dihydroxy ketones. Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1989**, *30*, 3323.

(3) Alder, R. W.; Baker, R.; Brown, J. M. *Mechanism in Organic Chemistry*; Wiley-Interscience: New York, 1970; p 295.

(4) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154. Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. O. *J. Am. Chem. Soc.* **1976**, *98*, 269. Sharpless, K. B.; Singer, S. P. *J. Org. Chem.* **1976**, *41*, 2504; **1978**, *43*, 1448. The Sharpless reagent TsN=Se=NTs has not been previously treated with trialkylsilyl enol ethers.

(5) The X-ray crystallographic structure determination of **7** was carried out by Dr. V. Lynch (Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712). It clearly shows the TsNH group locked in an axial position; $A^{1,3}$ strain probably prevents conformational relaxation to an equatorial configuration.

(6) Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett.* **1974**, 4319. Hassner, A.; Reuss, R. H.; Pinnick, H. W. *J. Org. Chem.* **1975**, *40*, 3427. Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1978**, *43*, 1599. Rubottom, G. M.; Marrero, R. I. *J. Org. Chem.* **1975**, *40*, 3783. Rubottom, G. M.; Gruber, J. M.; Boeckman, R. K., Jr.; Ramaiah, M.; Medwid, J. B. *Tetrahedron Lett.* **1978**, 4603.

adducts at the amino group without interference from the adjacent carbonyl functionality.[7] Correspondingly the allylic bromide **8** opens the door to a wide range of oxyallyl cation chemistry.[8]

This new facet of truly kinetic carbonyl chemistry should reveal a broad spectrum of complementary synthetic transformations that can be anticipated to take place with exceptional stereoelectronic control. These possibilities are being studied.

Acknowledgment. Dr. Mugrage thanks the National Institutes of Health for the award of a postdoctoral fellowship. Dr. Vince Lynch is gratefully thanked for X-ray structural determinations.

Supplementary Material Available: General spectral details for compounds **3–8** and **17–22**, details of the X-ray structure determination of **7**, tables of fractional coordinates, isotropic thermal parameters, anisotropic thermal parameters, bond lengths, and bond angles for $C_{23}H_{39}NO_3SSi$, and atom labeling and unit packing diagrams for $C_{23}H_{39}NO_3SSi$ (14 pages). Ordering information is given on any current masthead page.

(7) 2-Aminocyclohexanone readily self-condenses on treatment with acids or bases to give after oxidation octahydrophenazine. Smith, P. A. S. *J. Org. Chem.* **1960**, *25*, 2047.

(8) Giguere, R. J.; Hoffmann, H. M. R.; Hursthouse, M. B.; Trotter, J. *J. Org. Chem.* **1981**, *46*, 2868.

Coupling of a 2-Oxacyclopentylidene and a Phosphonium Ylide Ligand at Platinum. Migratory Insertion of a Fischer Carbene into a Metal Alkyl Bond

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Received September 5, 1989

Intramolecular migratory insertion reactions involving transition-metal carbene and σ-carbon ligands are intermediate in several interesting organometallic transformations in which new carbon–carbon bonds are formed.[2] These insertions typically involve highly reactive carbene-alkyl precursors generated in situ; in only one case has a complex which undergoes subsequent insertion chemistry been isolated.[2h] Here we report an isolable 2-oxacyclopentylidene bis(phosphonium ylide) complex of platinum that undergoes a facile migration of one phosphonium ylide ligand to the carbene. This process represents both unique reactivity for the platinum oxacyclopentylidene system[3] and, to our knowledge, the first observation of a migratory insertion process involving a phosphonium ylide ligand. In addition, the ultimate organic product of this reaction is a patented synthetic intermediate prepared in low yield by conventional organic methodology.

We considered the bis(phosphonium ylide) complex **1** (Scheme I), prepared by treatment of $(COD)Pt(CH_2I)_2$ (COD = 1,5-cyclooctadiene) with excess triphenylphosphine,[4] to be an ideal template on which to probe the nature and reactivity of the phosphonium ylide ligand. While the synthesis of ylide complexes has been extensively investigated,[5] substantially less is known about the reactivity of coordinated phosphonium ylides.[6,7] To provide an open coordination site for binding a potentially reactive ligand, abstraction of both iodide atoms was accomplished by using $AgBF_4$ in anhydrous acetonitrile, giving acetonitrile complex **2** in 82% yield after recrystallization from CH_2Cl_2/benzene.[8] The cis orientation of the ylide ligands follows from the observation of three signals in the ^{31}P NMR spectrum. The coordinated ace-

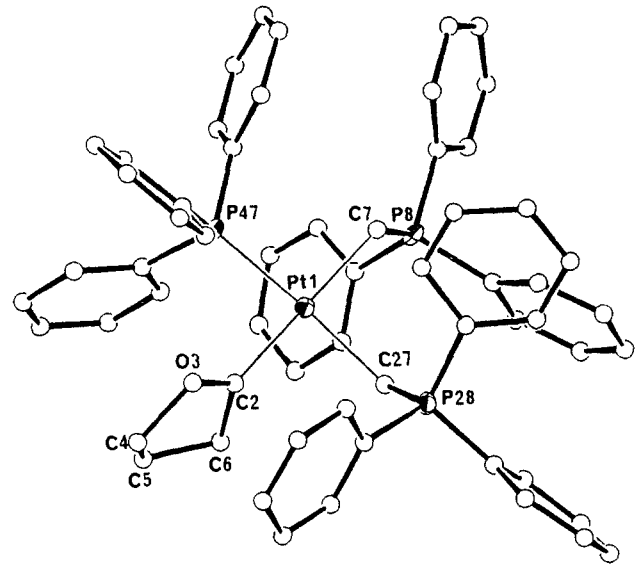
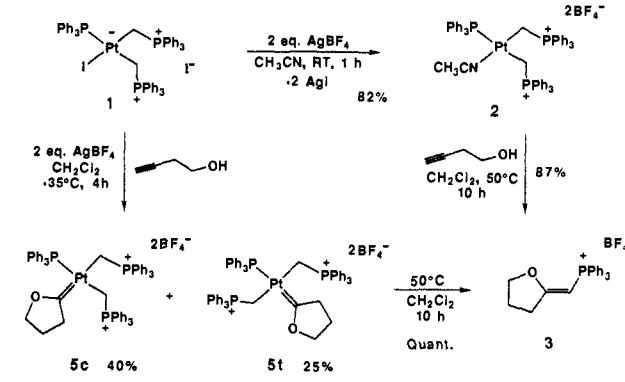


Figure 1. ORTEP drawing of **5c** (the hydrogen atoms have been omitted for clarity). Selected bond distances (Å): Pt(1)–C(2), 1.990 (22); Pt(1)–C(7), 2.122 (21); Pt(1)–C(27), 2.092 (22); Pt(1)–P(47), 2.299 (6); C(2)–O(3), 1.325 (27); C(7)–P(8), 1.772 (21); C(27)–P(28), 1.783 (22). Selected bond angles (deg): Pt(1)–C(2)–O(3), 123.2 (17); Pt(1)–C(2)–C(6), 123.2 (17); O(3)–C(2)–C(6), 113.5 (20); C(2)–Pt(1)–C(27), 90.2 (9); C(2)–Pt(1)–P(47), 87.5 (7); P(47)–Pt(1)–C(7), 91.1 (6); C(7)–Pt(1)–C(27), 91.1 (8); C(2)–Pt(1)–C(7), 174.9 (9); C(27)–Pt(1)–P(47), 177.4 (6). Least-squares acute plane angle (deg): ((Pt(1)–C(2)–O(3)–C(6))–((Pt(1)–C(7)–C(27)–P(47), 61.75. Final residuals: $R(F) = 0.068$ and $R_w(F) = 0.060$.

Scheme I



(1) Du Pont Young Faculty Awardee, 1988–1989. Union Carbide Innovation Recognition Program Awardee, 1989.

(2) (a) Van Leeuwen, P. W. N. M.; Roobeek, C. F.; Huis, R. *J. Organomet. Chem.* **1977**, *142*, 243. (b) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984. (c) Thorn, D. L. *Organometallics* **1985**, *4*, 192. (d) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. Jernakoff, P.; Cooper, N. J. *J. Am. Chem. Soc.* **1984**, *106*, 3026. (e) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278. (f) Kletzin, H.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46. (g) McCrindle, R.; Arsenault, G. J.; Farwaha, R.; Hampden-Smith, M. J.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1986**, 943. (h) Stenstrom, Y.; Koziol, A. E.; Palenik, G. J.; Jones, W. M. *Organometallics* **1987**, *6*, 2079, and references therein. Conti, N. T.; Jones, W. M. *Organometallics* **1988**, *7*, 1666. (i) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 4129.

(3) (a) Chisholm, M. H.; Clark, H. C. *J. Chem. Soc., Chem. Commun.* **1970**, 763. (b) Chisholm, M. H.; Clark, H. C. *Inorg. Chem.* **1971**, *10*, 1711. (c) Chisholm, M. H.; Clark, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 1532. (d) Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res.* **1973**, *6*, 202.

(4) Hoover, J. F.; Stryker, J. M. *Organometallics* **1988**, *7*, 2082.

(5) An extensive listing of references is given in ref 4.

(6) (a) Reviews: Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1. (b) Recent investigations: Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1154. Alt, H. G.; Hayen, H. I. *J. Organomet. Chem.* **1986**, *316*, 301.

(7) Depending on metal, oxidation state, and ligand set, the phosphonium ylide ligand may be nucleophilic at carbon, reflecting polarization of the metal–carbon bond, or electrophilic at carbon, reflecting polarization of the carbon–phosphorus bond. In the former case, reactivity involving the intact ylide ligand is expected; in the latter, phosphine loss and reaction of the resultant methylene ligand should be observed.

(8) Complete spectroscopic and analytical data is provided as Supplementary Material.

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